

Electrochromic properties of tungsten–molybdenum oxide electrodes

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Tungsten oxide and molybdenum doped tungsten oxide electrochromic films have been electrochemically prepared from a metal peroxide bath and experimentally tested. They were characterized by electrical and optical methods, using cyclic voltammograms and calculating the charge capacity as a function of the number of deposition cycles.

The color of the electrochromic WO_3 film is strongly altered by doping it with molybdenum. Electrochromic W–Mo oxide films were fabricated by adding different percentages of molybdenum to tungsten oxide, ranging from 0.5% to 7% weight of deposition solution. Normal optical transmittance was also measured and evidence is given of different behavior of the switching for oxidation and reduction cycle, so that coloration occurs in a shorter time than the bleaching. The time constant of the process tends to increase as a function of the molybdenum oxide doping concentration.

1. Introduction

Electrochromic materials are very promising to realize smart windows, displays and for large-area applications [1–3]. Experimental research over the past several years has been devoted to the perfection of the electrochromic and associated electrodes including the optimization of the switching time and the chromatic properties of the electrodes in solid state electrochromic devices.

A powerful and experimented technique, in this sense, is the insertion of dopant ions in the crystalline lattice of the electrochromic material, in order to modify its physico-chemical properties. One of the most studied and promising material

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appears to be tungsten oxide (WO_3) [4–7]. The possibility to improve the dynamical answer of the transition by doping, has been widely discussed in literature. The use of lithium as dopant [8,9] seems to improve the infrared reflectance, while the use of molybdenum [10–12] permits to modify the chromatic properties.

The electrochemical deposition technique, useful for the preparation of large and uniform electrochromic layers, appears very adapt for the addition of dopant elements.

2. Experimental

An investigation was made on the electrical and optical characteristics of electrochromic (EC) tungsten oxide and molybdenum doped tungsten oxide films. The films were electrochemically prepared from a metal peroxide bath.

Tungsten oxide EC films were deposited electrochemically from 0.1 M solution of tungsten peroxide obtained by preliminar dissolution of 3 g of tungsten metallic powder in 200 cm³ of aqueous solution containing 2% H_2O_2 [13–15]. The substrates were indium tin oxide (ITO) glass electrodes. A cyclic triangle waveform potential ranging from -400 up to -700 mV versus a standard calomel electrode (SCE) with a scanning rate of 100 mV/s was used per deposition. The ITO conducting glasses (2×4 cm) were furnished by Donnelly Corporation Holland (MI, USA) and had a sheet resistance of $10 \Omega/\square$. The voltammetric characteristic during deposition was recorded. In fig. 1 the n -cyclic I - V pattern is shown for tungsten oxide films, deposited respectively with $n = 5, 20, 50$ and 100 cycles. As shown in fig. 1, the exchanged charge, that can be calculated by the loop area, reaches its maximum when deposition utilizes a scan number between 50 and 100.

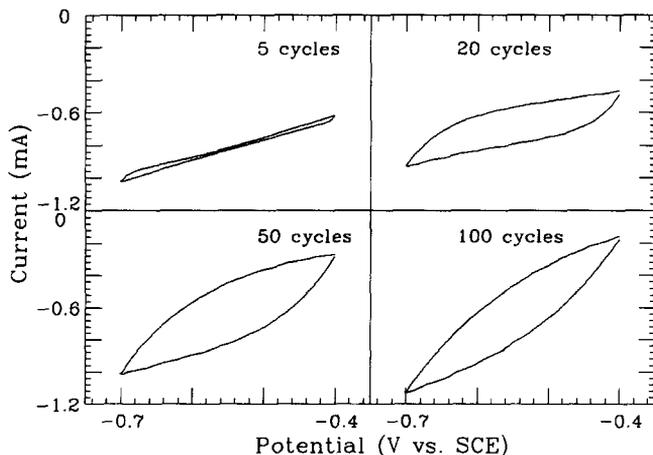


Fig. 1. Voltammetry of EC tungsten oxide deposition process from a peroxide solution for a different number of cycles. The active electrode area is 5 cm².

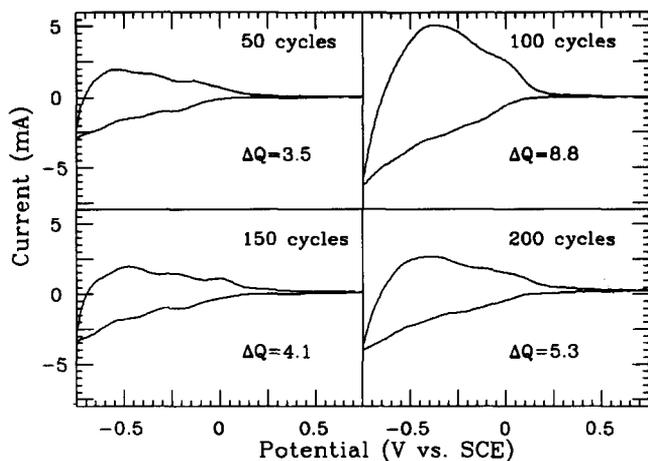


Fig. 2. Voltammetry in 0.1 M H_2SO_4 of tungsten oxide electrodes deposited with a different number of cycles. The scan rate is 50 mV/s. The charge capacity, ΔQ (in mC/cm^2) for each curve is indicated.

The electrode properties were measured in 0.1 M H_2SO_4 , using a calomel reference and a platinum wire counter electrode. Typical cyclic voltammograms are shown in fig. 2. A cyclic triangle potential ranging from 0.6 to -0.6 V and a scan rate of 50 mV/s was used. During each cycle the EC layer switches from the colored to the bleached phase and vice versa. Biasing potentials were generated by a PAR 173/276 potentiostat, driven by a IEEE-488 Data Acquisition System. Both current and voltage were monitored during the deposition and recorded by a Linseis LY 1600 X-Y recorder. The curve in fig. 2 for 100 deposition cycles exhibits the highest charge capacity ($8.8 \text{ mC}/\text{cm}^2$). The calculated charge capacity for each curve is indicated. The active electrode area is $2.5 \text{ cm} \times 2 \text{ cm}$, because a portion of ITO glass substrate, used for electrical contact, is uncoated.

Normal optical transmittance, over the 350 to 1100 nm wavelength range, was measured in situ in 0.1 M H_2SO_4 solution. Optical measurements were made using a Perkin-Elmer 'Lambda 2' UV/VIS spectrophotometer equipped with a special quartz cell ($1 \times 5 \times 5 \text{ cm}$, path length 1 cm). This cell allows the insertion of the $2 \times 4 \text{ cm}$ EC films normally to the light beam and also a platinum wire counter-electrode and a micro SCE reference electrode. The EC layer was biased at 600 mV to obtain the bleached state (fig. 3), and at -600 mV for the colored one (fig. 4). The curves show the optical transmittance for samples prepared using a different number of scans for the deposition. The bleached phase is not influenced significantly to 150 deposition cycles. Increased absorbance is evident only for sample (d) at 200 cycles, for wavelengths greater than 800 nm. The small variations observed in the interference fringes are due to differences in the film thickness. The position of the interference fringes indicated the thickness of the films. By recording the position of maxima as a function of wavelength, we obtained a typical value of about 2000 \AA for 100 deposition cycles. Large differences of the interference maxima are noticed in the optical transmittance for the same elec-

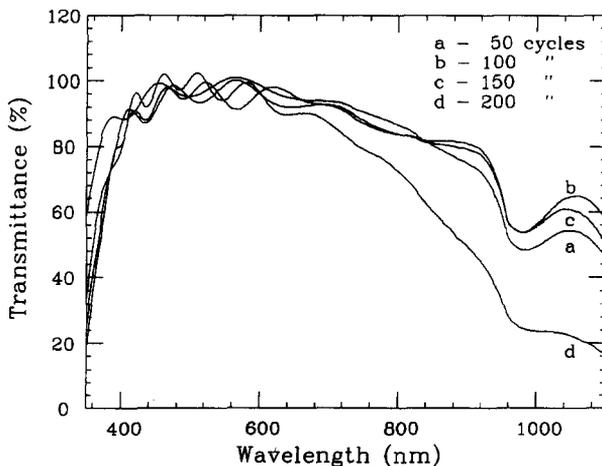


Fig. 3. Normal transmittance of EC tungsten oxide films of various thickness in the bleached state. The films are biased at 600 mV versus SCE and are placed in a microcell containing 0.1 M H_2SO_4 electrolyte.

trodes in the colored phase (see fig. 4), they are related to the effective thickness of the optically active electrochromic layer.

An ion backscattering spectrometry (IBS) analysis, using 2 MeV He^+ ions, was carried on electrochromic electrodes in order to verify thickness [16]. A typical IBS spectrum is shown in fig. 5. The arrows indicate the energy of ions backscattered by atoms of different species (W and Sn). The width of the box at higher energy

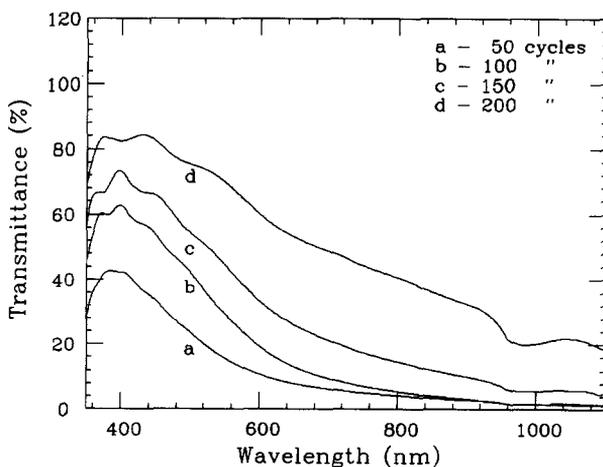


Fig. 4. Normal transmittance of EC tungsten oxide films of various thickness in the colored state. The films are biased at -600 mV versus SCE and are placed in a microcell containing 0.1 M H_2SO_4 electrolyte.

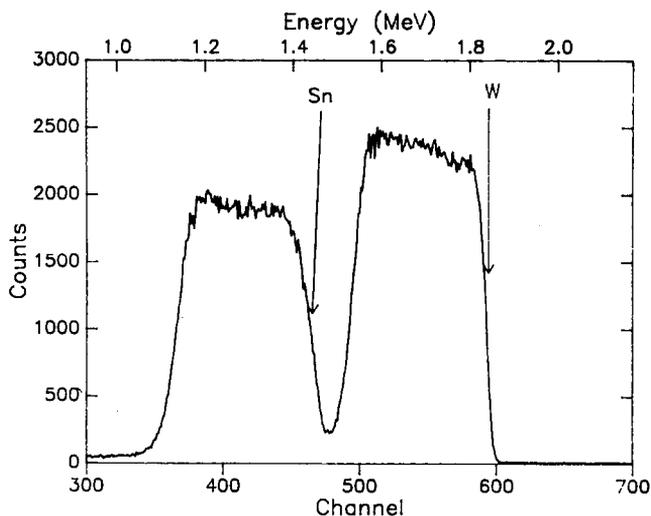


Fig. 5. He^+ ions backscattering spectrum of a WO_3 EC layer deposited on ITO substrate. The arrows indicate the energy of ions backscattered by surfacial atoms of W and Sn. The width of the two boxes are related to the thickness of the WO_3 and ITO layers. The WO_3 layer was found to have 2350 Å thickness, and the SnO_2 layer was found to have 4000 Å thickness.

represents the ion energy loss in the WO_3 layer, strongly dependent on the thickness of the film. The value of the thickness was found from IBS to be about 2350 Å for 100 deposition cycles. The width of second box (at lower energies) is proportional to the thickness of the ITO layer (about 4000 Å). Signals coming from indium and tin cannot be resolved due to the similar mass of the two elements, so that the energy of backscattered ions is nearly the same. No substantial difference can be observed in the spectra obtained from tungsten oxide samples doped with molybdenum, at least up to a Mo concentration value of 7%.

As a consequence of the voltammetry charge capacity and of the optical transmittance, we chose 100 cycles for film deposition. A light blue coloration was observed during the film growth. The electrodes were rinsed successively in distilled water and thermally treated for 1 h at 130°C.

3. Electrochromic properties of W–Mo alloys

To alter the color of electrochromic WO_3 films we doped them with molybdenum. Tungsten–molybdenum oxide films were fabricated by adding to the solution previously described for WO_3 deposition, different quantities of a 0.1 M molybdenum oxide solution obtained dissolving 1 g molybdenum metallic powder in 10 ml of 35% H_2O_2 . The molybdenum concentration we report thereafter is coincident with the percentage in weight of molybdenum dissolved in the electrolytical solution. The parameters for the electrochemical deposition were the same as for

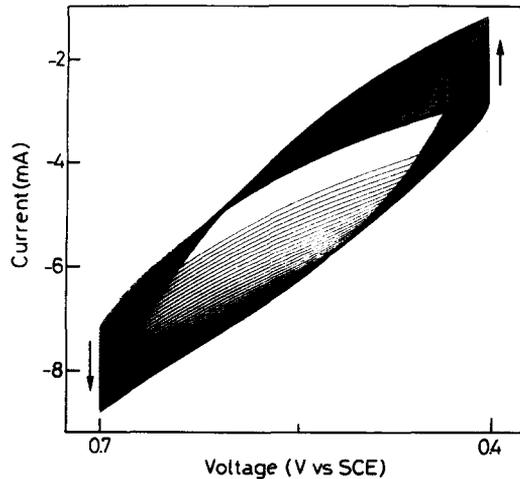


Fig. 6. Voltammetry of an EC WO_3 film doped with 0.5% Mo oxide, deposited from a peroxide solution. The scan rate is 100 mV/s. The arrows indicate the evolution in time of the deposition cycle.

the undoped tungsten oxide films. We noted that with an increased percentage ($> 10\%$) of molybdenum in the film, weaker adhesion to the substrate occurred, in fact an electrical or thermal shock can be responsible of film peeling.

Figs. 6 and 7 show the voltammetry of the electrochromic W-Mo oxide alloy deposition process, respectively for a 0.5% and 7% Mo oxide concentration. The arrows indicate the evolution in time of the voltammetry pattern. A decrease in exchanged charge per cycle is evident when the Mo concentration is increased.

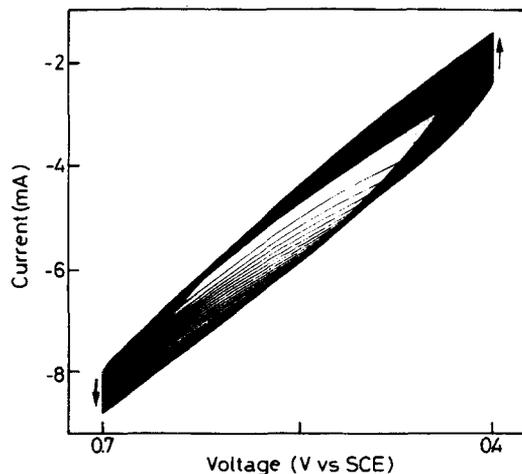


Fig. 7. Voltammetry of an EC WO_3 film doped with 6% Mo oxide deposition processed from a peroxide solution. The scan rate is 100 mV/s. The arrows indicate the evolution in time of the deposition cycle.

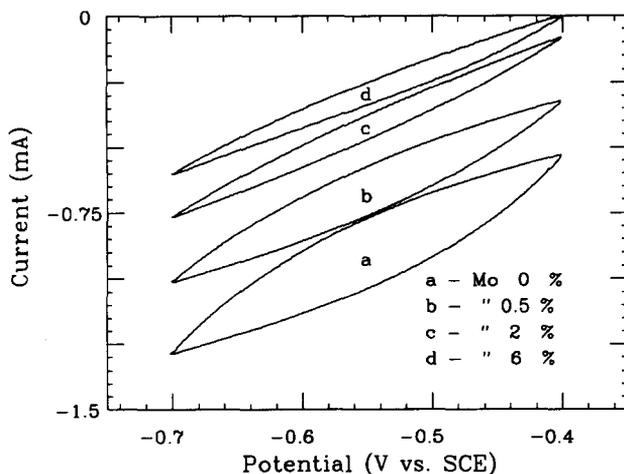


Fig. 8. I - V pattern of the 100th deposition cycle for samples containing different percentages of Mo oxide.

This means there is a different amount of deposited layer per cycle. In fig. 8 this effect is clearly sketched. The pattern of the last deposition cycle (the 100th) is shown for samples containing a different percentage of molybdenum.

Fig. 9 shows the charge-discharge relationship for two different EC electrodes in 0.1 M H_2SO_4 . The applied potential was a dc triangle potential shown in the inset. The charge and discharge branches of the solid line curve, obtained for an undoped sample, show that the current goes to the zero value within the time

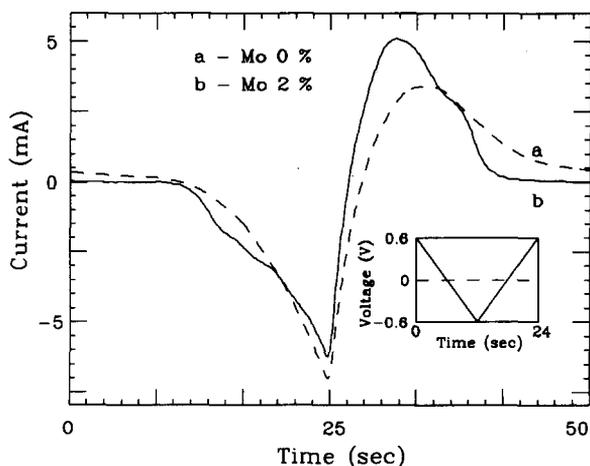


Fig. 9. Charge-discharge relationship for two different W-Mo oxide EC films in sulfuric acid. The applied potential was a triangle potential, shown in the inset. The scan rate is 50 mV/s and the active area is 5 cm².

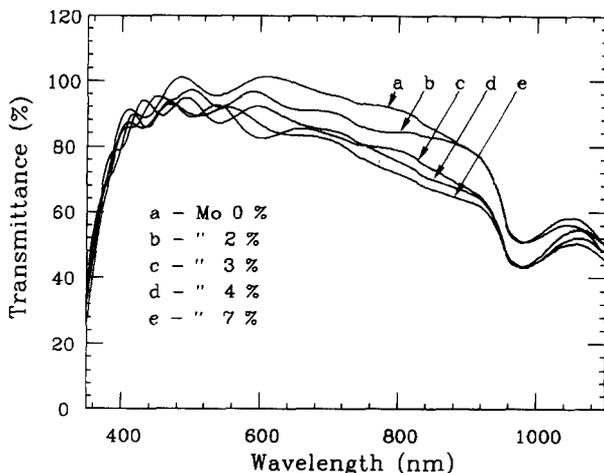


Fig. 10. Normal transmittance for EC tungsten oxide films containing various percentages (indicated) of Mo oxide, in the bleached state. The films are biased at 600 mV versus SCE in a cell containing 0.1 M H_2SO_4 .

interval of the sweep. The dashed curve, obtained with a sample doped with 2% molybdenum, shows two slightly different behaviors for oxidation and reduction processes. The oxidation currents reach the zero value in a longer time and the amplitude of the oxidation peak reduces with increasing molybdenum concentration.

Transmittance data in the bleached state are shown in fig. 10 for several samples prepared with different Mo concentrations (between 0% and 7%). The transmittance in the oxidized form of the electrochromic film is not substantially altered by the Mo presence, because no significant variations of transmittance are noted up to 1100 nm. The same data for the colored state, reported in fig. 11, show a different behavior. In the visible region a larger percentage of Mo shows a decrease of transmittance. This tendency is reversed in the infrared region where the films labelled with e, f and g exhibit a lower absorbance. The dip close to 1000 nm is due to sulfuric acid absorption. A flatter curve shape is observed for the samples with greater doping. This behavior shows another significant effect, the change in film color in the reduced phase. While the undoped WO_3 switches from transparent to blue, by doping it with Mo oxide, the coloration shifts to grey (see figs. 12 and 13). Also this effect is shown in fig. 14 where the transmittance, in the colored state, is reported as a function of Mo concentration at various wavelengths (compare the decreasing curve obtained at 400 nm, with the increasing one obtained at 1100 nm).

Photopic (T_p) and solar (T_s) transmittance in the two EC states of the films were calculated and plotted in fig. 15 as a function of the dopant Mo concentration. No relevant variation in the values of T_p and T_s in the bleached state is observed when Mo doping concentration ranges from 0% up to 8%. The most significant effect is

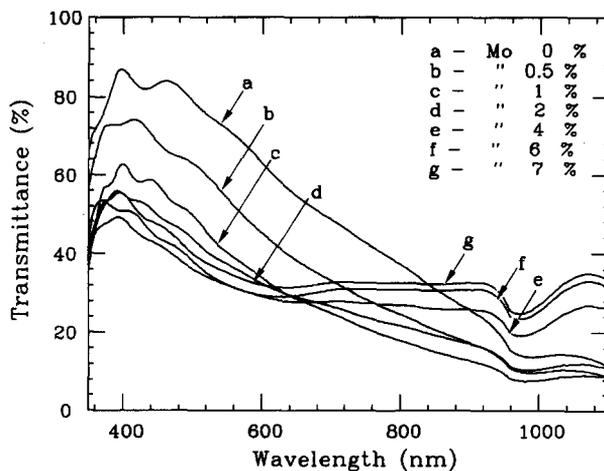


Fig. 11. Normal transmittance for EC tungsten oxide films containing various percentages (indicated) of Mo oxide, in the colored state. The films are biased at -600 mV versus SCE in a cell containing 0.1 M H_2SO_4 .

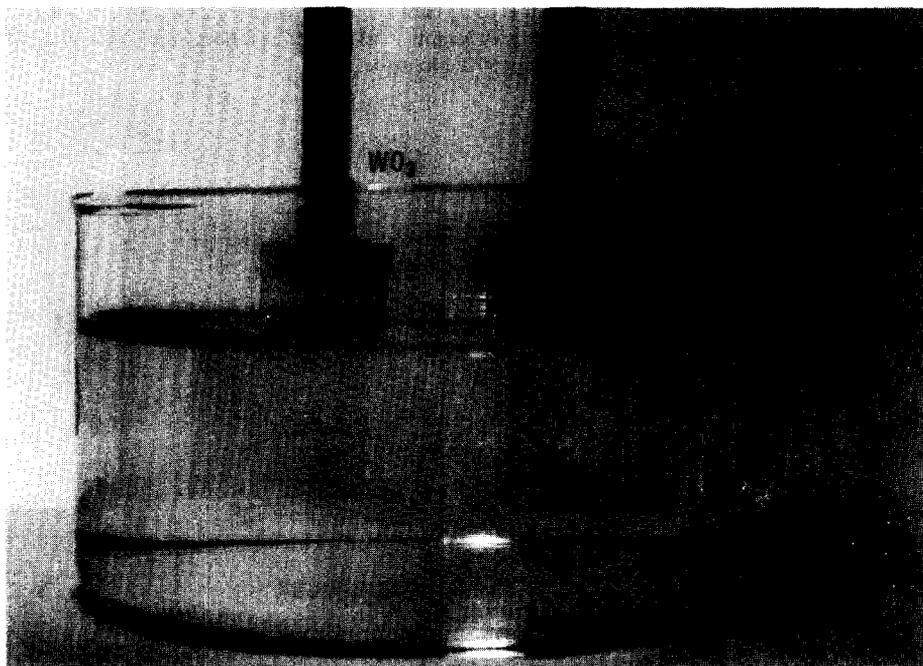


Fig. 12. Two EC films, in the bleached state, in H_2SO_4 bath. The sample on the left (marked with a dot) is an undoped WO_3 film on ITO glass, the sample on the right (marked with two dots) refers to a WO_3 film containing 6% Mo oxide.

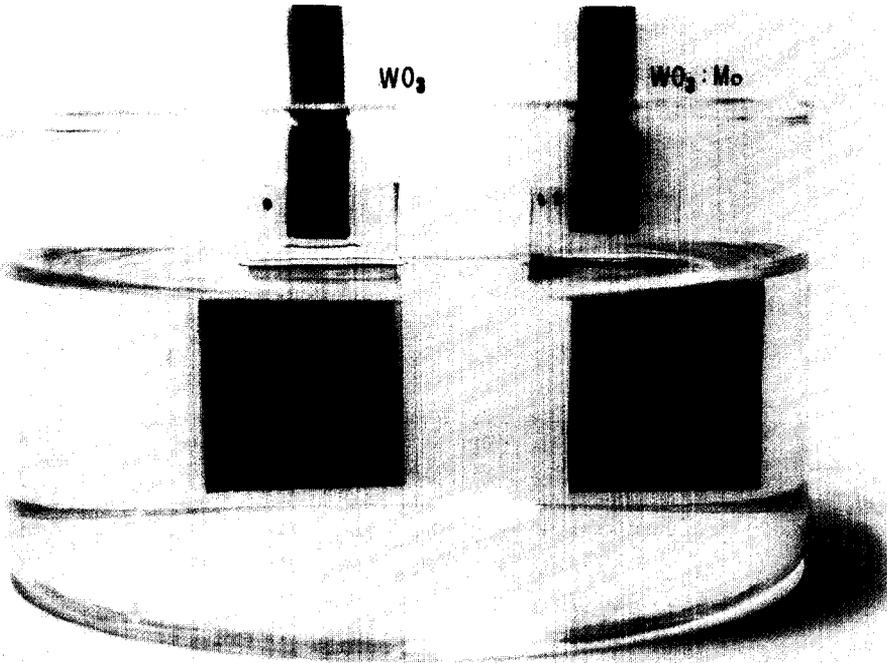


Fig. 13. Two EC films, in the colored state, in H_2SO_4 bath. The blue sample marked with a dot refers to undoped WO_3 film on ITO glass, while the grey sample marked with two dots, refers to a WO_3 film containing 6% Mo oxide.

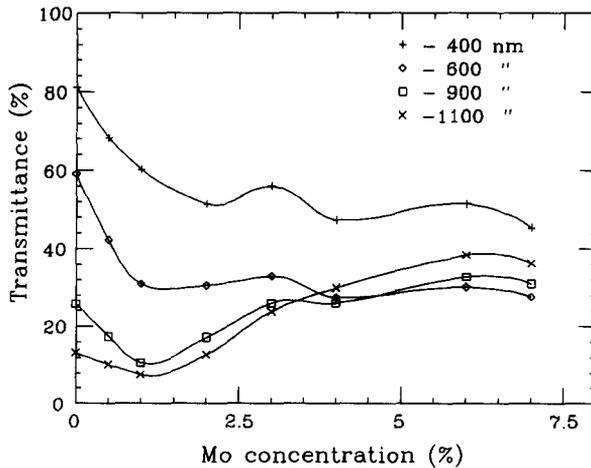


Fig. 14. Normal transmittivity of W-Mo oxide films, in the colored state, versus the percentage of dopant Mo concentration. The various curves are for different wavelengths.

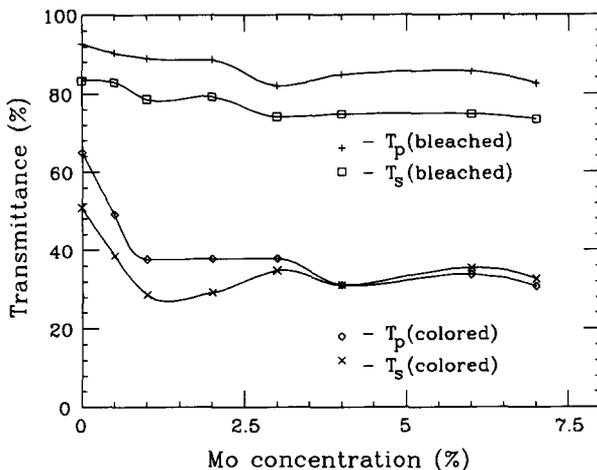


Fig. 15. Calculated photopic (T_p) and solar (T_s) transmittance, for the bleached and colored condition of the EC W–Mo oxide films, as a function of dopant Mo concentration.

a substantial decrease (about 30%) of the photopic and solar transmittance, in the colored state, followed by an almost flat region, by the addition of a low percentage of molybdenum (less than 2%).

4. Discussion of the EC switching rate

The EC W–Mo oxide samples were successively tested under cyclic potential conditions, in order to observe the transmittance behavior in the two states. In fig. 16 we report the transmittance versus time for samples containing different percentages of molybdenum dopant. The curve marked with a refers to the undoped sample, while the curves b, c and d refer to samples containing 0.5%, 3% and 6% of Mo respectively. The applied voltage has a trapezoidal waveform, with a period of 200 s, ranging from 600 mV to –600 mV, as shown in lower part. This type of waveform is used to avoid an excessive current during the EC transition which otherwise tends to degrade the active layer. The time constants of the process tend to increase as a function of Mo oxide concentration and, as a consequence, it is possible to detect a less marked optical transition at a fixed biasing waveform. In general, the switching time for oxidation is longer than the one for reduction, so coloration occurs in a shorter time than bleaching.

In order to explain this behavior the switching process has to be analyzed from a microscopic point of view. In fact, while the coloring is mainly governed by the properties of the interface between the EC material and the electrolyte that injects protons, the bleaching is governed by the proton and electron injection. During this latter phase, electrons move from the EC layer to the electrolyte, while protons diffuse towards the ITO. The flow of the current is limited only by the

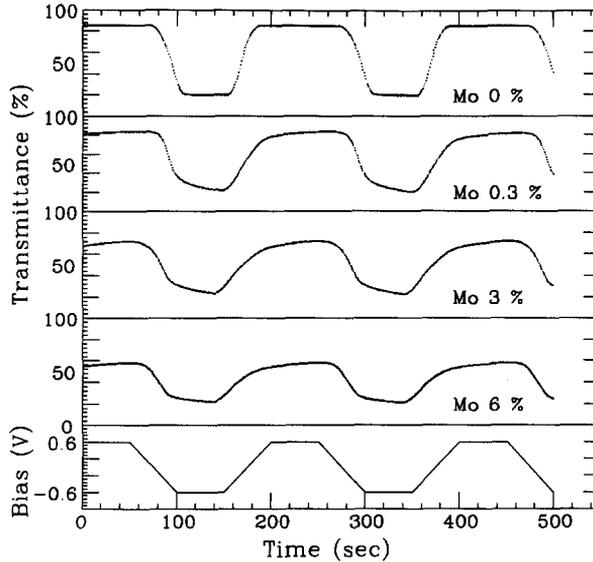


Fig. 16. Normal transmittance versus time for W-Mo oxide EC layers containing different percentages of Mo oxide. The molybdenum content of each samples is indicated. The applied potential has a trapezoidal form, with a period of 200 s, as shown in the lower plot.

presence of a proton space charge layer in the region adjacent to the electrolyte interface.

The gradient of proton concentration determines the behavior in time of the current flow. It is possible to calculate the diffusion constant of protons into the EC alloy. We utilized the MacArthur model [17] that permits the determination of the diffusion coefficient for protons moving in the EC lattice, following analysis of the current transient under a potential step. The model is similar to that used for one dimensional heat transfer. The experimentally measured quantity is the diffusion current i_d as a function of time, that can be expressed in an exponential form as:

$$i_d = \frac{n_e F A D 2C^0}{h} \sum_{n=0}^{\infty} \exp\left(-\frac{D\pi^2(2n+1)^2 t}{4h^2}\right), \quad (1)$$

where n is an integer, n_e is the number of positive charges on the diffusion species, F is the Faraday constant, A the area of the electrode, D the diffusion coefficient, t the time from the start of the diffusion process, C^0 the concentration of tungsten sites in the WO_3 lattice and h the diffusion length. The values of D and h may be found by noting that for sufficiently long times only the term with $n=0$ in the summation will be significant. By extrapolating to zero time, the current intercept in a semilog plot is proportional to the ratio D/h , while the ratio between the intercept and the slope of a straight line fitting the $i_d(t)$ curve, is proportional to h .

Following this method we plotted on a semilog frame the oxidation current flowing in a three-electrode cell versus time, under a step potential going abruptly from -600 to 200 mV. This abrupt potential step leads to a rapid peeling of the EC layer and the film comes off from the ITO substrate after only a few steps, because of the large currents in the cell. Analyzing this curve by the method previously described, we obtained for the proton diffusion coefficients of the oxidized EC phases values ranging from 8×10^{-7} cm²/s for the undoped sample to 1×10^{-7} cm²/s for a sample doped with 6% of Mo oxide. The values of D_{ox} (proton diffusion coefficient during the oxidizing reaction) decrease with the increasing of Mo percentage in the sample.

During the coloration process, the ITO layer and the electrolyte inject respectively electrons and protons into the WO₃ layer. Because WO₃ and counterelectrode are different materials, there will be an EMF between them proportional to their chemical potential difference. As the film colors, its chemical potential changes, to make the film more positive with respect to the counterelectrode. This EMF is directed opposite to the applied voltage and the current is limited by many different mechanisms, among which the presence of a barrier at the contacts injecting respectively electrons and protons is very important.

For times large compared to the characteristic time for proton diffusion, the expression giving the current exhibits the commonly observed dependence on the inverse square root of time, which is typical in the presence of a barrier. However the diffusion of protons in the film can significantly alter the coloring speed only at times short if compared with the diffusion time. In this case the diffusion

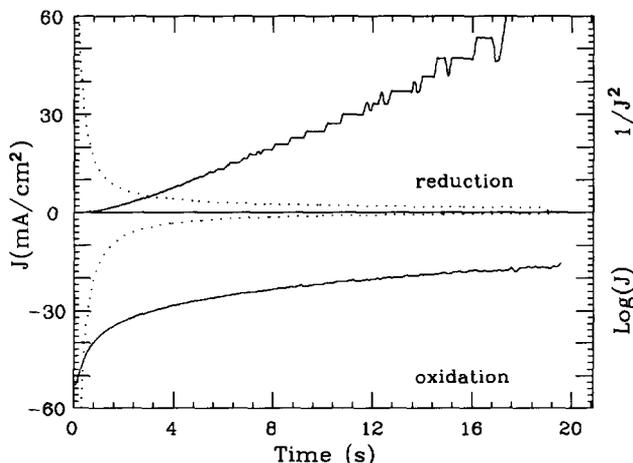


Fig. 17. Reduction and oxidation current densities (dotted curves) for a WO₃ sample doped with 1% Mo oxide. The applied potential is a step going from 200 mV to -600 mV for the reduction (coloration) and from -600 mV to 200 mV for the oxidation (bleaching). The solid curves show respectively the behavior of $1/J^2$ and $\log(J)$ versus time. These curves are utilized to calculate the diffusion coefficient of the protons into the EC layer.

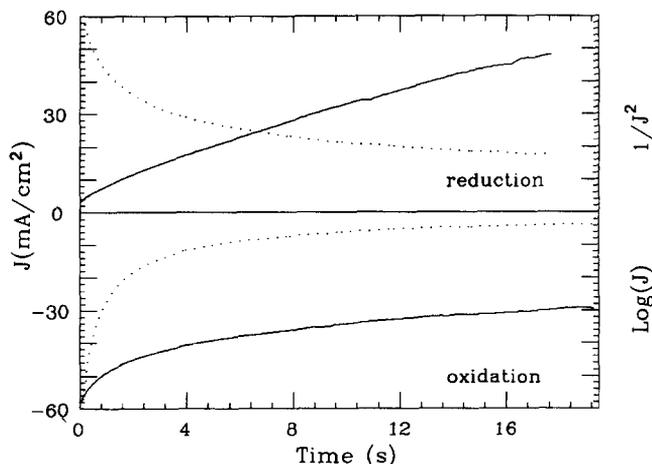


Fig. 18. The same as in fig. 17 for a WO_3 sample doped with 5% Mo oxide.

coefficient can be estimated by diffusion current i_d through the expression [18]

$$i_d = e\rho x_s A \sqrt{D/\pi t}, \quad (2)$$

where ρ is the tungsten atom density, e the electron charge and x_s is a constant of the order of 0.5.

We utilized expression (2) to estimate the diffusion coefficient for the reduction phase, analyzing the current transient induced by the application of a potential step going from -600 mV to 200 mV. The obtained values of D are comparable with those calculated for the oxidation phase. All values are in agreement with ones reported in the literature [18,19].

In figs. 17 and 18, reduction and oxidation current densities J (dotted curves) are reported for two samples doped respectively with 1% and 5% Mo oxide. The linear dependence of $1/J^2$ with time gives evidence that the behavior of the reduction current is well described by eq. (2). Similarly the linear dependence at large times of $\log(J)$ with time gives evidence that the diffusive model described by eq. (1) is working well for the oxidation state.

5. Conclusions

In summary, the transition-metal oxide films we prepared by electrochemical deposition exhibit good electrochromic properties. Adding of molybdenum, at least to a percentage of 2%, gives better film dynamical optical response, because it increases the switching range between the transmittivity values. In fact, while the photopic transmittance of the bleached state remains unaltered, its value changes from $T_p = 0.65$ to $T_p = 0.38$, in the colored phase, for two samples containing 0% and 2% molybdenum respectively.

A larger dopant concentration leads to a longer transition time for both processes. However the reduction process is always faster if compared with the oxidation one. Correspondingly there is evidence of a longer "memory" of each phase and of a decrease in the infrared absorbance.

The possibility to alter gradually the color of the EC film by controlling the molybdenum content, gives new perspectives in the development of EC devices. A clear evidence is given in the paper of a strongly different behavior of normal transmittance in the colored state for differently doped films. In fact, while the undoped samples exhibit only a large peak at 400 nm, responsible of the blue coloration, the increase of doping produces a flatter spectrum at visible and infrared region, which gives the grey coloration.

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